

## ORIGINAL PAPER

**Conjugated push–pull salts derived from linear benzobisthiazole:  
preparation and optical properties**

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*Dedicated to Professor Štefan Toma on the occasion of his 75th birthday*

A series of novel monomethylated salts derived from linear benzobisthiazole was prepared. The push–pull attributes of these new compounds are represented by a quaternised azolium cycle as the acceptor part at one end of the structure and the dialkylamino- or diarylamino-substituted benzene ring as the donor part at the opposite end. Both moieties are connected by a conjugated linker consisting of one or two double bonds. Such dipolar structures are promising candidates for non-linear optical materials. The quantum-chemical indices describing linear and non-linear optical properties were obtained from semi-empirical calculations. The relationships between the chemical structure and non-linear optical properties of the cations studied were obtained. Effective conjugation was confirmed by measuring the optical properties in the UV-VIS region.

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**Keywords:** heterocycles, thiazolium salts, conjugation, non-linear optics, condensation**Introduction**

Organic heterocyclic compounds with a push–pull structure are noted for their wide range of applications as chromophores in non-linear optics (NLO), in the second harmonic generation (SHG) (Zhang et al., 2001), molecular probes (Fox, 1992), fluorescent markers (Lakowicz, 1994), organic light-emitting diodes (OLED) (Balaganesan et al., 2003), or photovoltaic cells (Loudet & Burgess, 2007). A typical push–pull organic chromophore consists of a polar A- $\pi$ -D structure with a planar  $\pi$ -system end-capped with a strong electron donor (D) and a strong electron acceptor (A). These systems use the following conventional substituents: dialkylamino or diarylamino groups as donors and nitro, cyano, or carbonyl groups as acceptors. The special set of D- $\pi$ -A molecules comprises heteroaromatic cations as the acceptor part; the heterocycles in most use are pyridinium, tetrazolium, acridinium, and benzothiazolium fragments. Conjugated benzothiazolium salts

are known and in commercial use, mainly as cyanine dyes (Thioflavine T, Thiazole Orange, Basic Blue 41) (Mojzych & Henary, 2008). Some D- $\pi$ -A benzothiazolium salts show antibacterial and anthelmintic effects (dithiazanine). The NLO properties of benzothiazolium salts, especially the unique two-photon absorption parameters, were demonstrated (Hrobáriková et al., 2010). In an effort to enhance NLO response, the benzothiazole part of the molecule was replaced with a more robust linear benzobisthiazole backbone which can occur in two isomers with axial or central symmetry. This structure renders it possible to prepare one- or two-armed condensation products. A further possibility for enhancing the acceptor capacity of the heterocyclic unit is alkylation of one or both of the heterocyclic nitrogen atoms. In this article, we focus on the synthesis and study of monomethylated salts derived from linear centrosymmetric benzobisthiazole and its one-armed condensation products with donor-substituted aromatic aldehydes. The electron donor part of the de-

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